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Energy Transfer in Polystyrene Nanoparticles with Encapsulated 2,5-Diphenyloxazole

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As the first step to design nanosystems for X-ray excited sensitising of singlet oxygen, nanoparticles of polystyrene (PS NP) and polystyrene with encapsulated diphenyloxazole molecules (PS-PPO NP) were synthesized. Inside the PS-PPO NP, the electronic excitation energy transfer from polystyrene matrix to encapsulated PPO molecules takes place; efficiency of such transfer was roughly estimated to be about 0.37. X-ray stimulated luminescence of PS-PPO NP was registered.

Introduction

Photodynamic therapy is the method for the treatment of cancer, where the photosensitizer excitation by the light leads to the generation of singlet oxygen that is toxic for the tumour tissue [1]. But despite of several advantages, the drawback of this method is the very small depth of the light penetration into the tissue [2]. Thus the idea of creating X-ray excited sensitizers composed of scintillating and photosensitizing parts with the electronic excitation energy transfer (EEET) from the first to the last one seems attractive [3]. Last years, several nanosystems based on this concept were described with various materials used as scintillators, various photosensitizer molecules and different ways of binding them to a system [2, 4-7]. In the frames of this concept, the X-ray stimulated luminescence of the porphyrin sensitizer was demonstrated for the nanoparticles containing polystyrene (PS), vinylpyridine, 2,5-diphenyloxazole (PPO) and hematoporphyrin [8]. The energy transfer processes were supposed for that system, but not studied and not proved. Here, as the first step to designing of more complex and efficient nanosystems for X-ray excited sensitizers of singlet oxygen, polystyrene-diphenyloxazole nanoparticles (PS-PPO NP) were synthesized; EEET process in such systems was studied and X-ray stimulated fluorescence from the PS-PPO NP was registered.

Experimental part

Synthesis of nanoparticles

A microemulsion polymerization was employed for the synthesis of PS NP as well as for incorporation of PPO into PS nanoparticles [8-10]. Latex beads containing organic compound were synthesized directly by the polymerization of a mixture of styrene and PPO with potassium persulfate (KPS) as initiator in a micellar aqueous solution of sodium dodecylsulfate. Namely, synthesis of PS NP and PS-PPO NP was performed as follows.

PS NP. Styrene was polymerized in a micellar aqueous solution of sodium dodecylsulfate (SDS) with potassium peroxydisulfate (KPS) as initiator: 2g styrene was added slowly over a period of 1.5 hours to a vigorously stirred solution of 0.01 g NaH_2PO_4, 0.2 g SDS and 0.01 g KPS in 10 ml of water at 70°C in argon atmosphere. The mixture was stirred for an additional 3 hours at 70 °C and for 1 h at 90 °C. The mixture was cooled to room temperature and dialyzed during 48 hours using cellulose membrane with MWCO 3 500Da.

PS-PPO NP. Styrene was polymeryzed in a micellar aqueous solution of sodium dodecylsulfate (SDS) with potassium peroxydisulfate (KPS) as initiator: a mixture of 2g styrene and 0.09 g 2,5-diphenyloxazole (PPO) was added slowly over a period of 1.5 hours to a vigorously stirred solution of 0.01 g NaH_2PO_4, 0.2 g SDS and 0.01 g KPS in 10 ml of water at 70 °C in argon atmosphere. The mixture was stirred for an additional 3 hours at 70 °C and for 1 h at 90 °C. The mixture was cooled to room temperature and dialyzed during 48 hours using cellulose membrane with MWCO 3 500Da.

Characterization of nanoparticles

Particle size distributions were studied by the dynamic light scattering (DLS) technique using Zetasizer Nano ZS (Malvern Instruments) apparatus (**Figure 1**). For the obtained SDS-coated PS NP, intensity distribution of the hydrodynamic diameter gave main maxima at 84±4 nm (about 93% of intensity) and 3.0±0.7 nm (about 5%), and for the PS-PPO NP such maxima were at 74±1 nm (about 86% of intensity) and 7.2±0.3 nm (about 13.5%). Since larger particles are known to make higher contribution to the DLS intensity, real average diameter values should be lower.

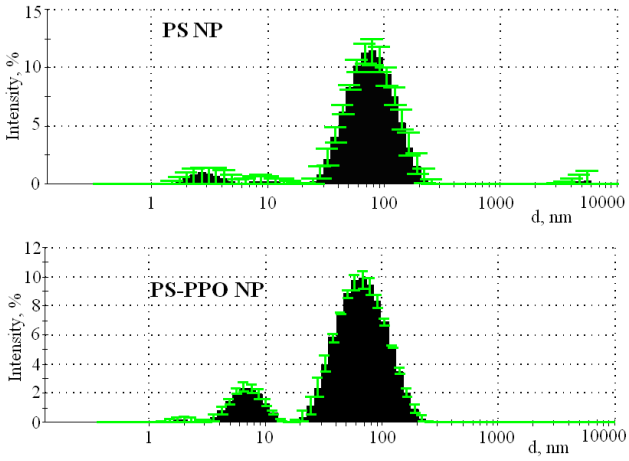

Figure 1. Distribution of DLS intensity for PS (top) and PS-PPO (bottom) nanoparticles, averaged for 5 measurements.

The size and morphology of the obtained nanoparticles were also characterized by

transmission electron microscopy (TEM) using a JEM-2010 microscope at an acceleration voltage of 200 kV (**Figure 2**). It could be seen from the figure that the obtained particles have spherical shape with the diameters about 20-40 nm.

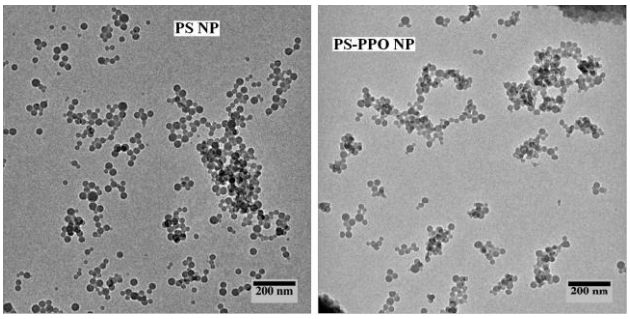

Figure 2. TEM images of PS (left) and PS-PPO (right) nanoparticles.

Spectral measurements

Absorption spectra were measured using Specord M40 spectrophotometer (Carl Zeiss, Germany). Fluorescence excitation and emission spectra were registered with the help of the Cary Eclipse fluorescent spectrophotometer (Varian, Australia). Absorption and fluorescence measurements were performed in 1cm × 1cm quartz cell at room temperature. Solutions of nanoparticles were dissolved in 1000 times in distilled water. PPO solution in distilled water free and in the presence of 0.5% SDS was studied for the comparison. The stock solution of PPO (10mM) was prepared in DMF; it was dissolved to the 10 μM concentration for the measurements; DMF admixture in the sample was thus 0.1%.

X-ray luminescence of the nanoparticles was excited by the total emission of the BHV7-Cu X-Ray tube (average energy of the quanta about 15 keV) and registered with the help of the laboratory designed equipment based on the DFS-2 monochromator (USSR) and PMT-106 photomultiplying tube (USSR).

Results and discussion

Absorption spectra of PS and PS-PPO nanoparticles, as well as PPO solution in water and in 0.5% SDS are presented at the **Figure 3**.

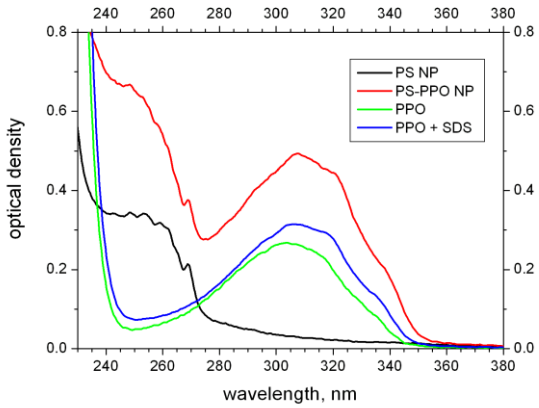

Figure 3. Absorption spectra of PS (black line) and PS-PPO (red line) nanoparticles dissolved in 1000 times in distilled water. Spectra of PPO (10 μM) in distilled water (green line) and in 0.5% water solution of SDS (blue line) are also provided.

It is seen from the figure that the spectrum of the PS-PPO NP consists of the bands corresponding to PS matrix and PPO. Comparison of the spectra of PS-PPO NP and PPO solution reveals that the band of PPO in the nanoparticle is shifted to the long-wavelength spectral region as compared to the free PPO one, besides the first spectrum is structured unlike the last one. This could be due to the fixation of the PPO molecule encapsulated in

the PS matrix. At the same time, the PPO band in nanoparticle is similar to the spectrum of PPO in the presence of SDS micelles. Thus fixation of PPO in the SDS shell of the nanoparticle cannot be excluded as well.

Fluorescence excitation and emission spectra of PPO and PS-PPO nanoparticles as well as of PPO in distilled water and in the presence of SDS micelles are presented in the **Figure 4**. Several observations and following conclusions could be made from this figure. First, perfect overlapping exists between PS NP emission and PPO excitation spectra that is the necessary condition for the EEET existence. Second, emission spectrum of the PS NP is structured with the main maximum near 310 nm that means that the separate styrene chains (and not styrene excimers) are mainly responsible for PS NP emission. Third, while non-structured emission spectrum was observed for the free PPO, for PPO in SDS presence some structure is present that should be connected with PPO fixation in SDS micelles. At the same time, in the case of PPO emission of PS-PPO NP (shoulder at 347 nm, bands at 367 and 383 nm) this structure is more strongly expressed as compared to PPO in SDS presence. This could be explained by the more rigid fixation of PPO upon its encapsulation in the polystyrene nanoparticle (though the more rigid PPO fixation in SDS shell covering the NP as compared to pure SDS micelle cannot be completely excluded as well). Fourth, the bands corresponding to PS absorption (229 and 264 nm) appear in an excitation spectrum of PPO emission upon its encapsulation into the NP, what means that the energy transfer (EEET) process takes place inside the nanoparticles from PS matrix (i.e. styrene chains) to encapsulated PPO molecules.

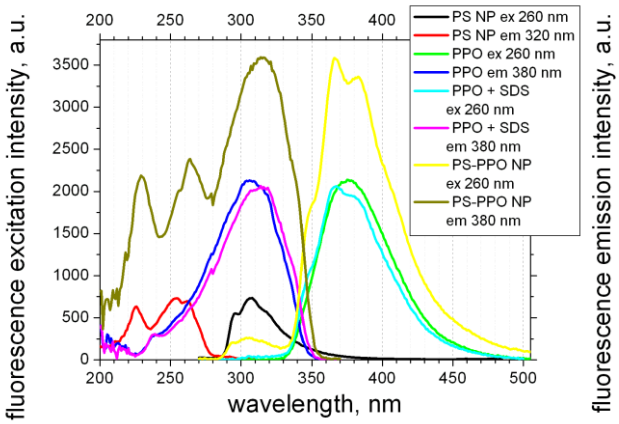

Figure 4. Fluorescence excitation (left; emission wavelengths indicated) and emission (right; excitation wavelengths indicated) spectra of PS NP and PS-PPO dissolved in 1000 times in distilled water. Spectra of PPO (10 μM) in distilled water and in 0.5% water solution of SDS are also provided. Fluorescence excitation spectra were normalized to corresponding emission spectra.

Efficiency of the EEET from the PS matrix to encapsulated PPO inside the PS-PPO NP, i.e. the ratio of the number of quanta transferred to PPO to this absorbed by PS matrix could be roughly estimated. For this, the EEET efficiency could be determined as $E_{EEET} = (N_{abs}^{PPO}/N_{abs}^{PS})\times(N_{emPPO}^{exPS}/N_{emPPO}^{exPPO})$, where N_{abs}^{PPO} and N_{abs}^{PS} are number of quanta absorbed by PPO and PS matrix respectively in the PS-PPO NP, and N_{emPPO}^{exST} and N_{emPPO}^{exPPO} are number of quanta emitted by PPO upon

excitation of styrene and PPO respectively. Further, it should be mentioned that for the PS-PPO NP, absorption of PS matrix at 260 nm is roughly equal to that of encapsulated PPO at 310 nm (**Figure 3**). Thus, $E_{EEET} = N_{emPPO}^{exPS}/N_{emPPO}^{exPPO} = I_{PS\text{-}PPO}^{ex260}/I_{PS\text{-}PPO}^{ex310}$, where $I_{PS\text{-}PPO}^{ex260}$ and $I_{PS\text{-}PPO}^{ex310}$ are fluorescence intensities of PPO emission in PS-PPO NP upon excitation of PS matrix (260 nm) and PPO (310 nm) respectively; from $I_{PS\text{-}PPO}^{ex260}$ the contribution corresponding to direct PPO excitation at 260 nm should be subtracted (using fluorescence excitation spectrum of PPO in SDS presence). Thus, calculation according to the above procedure (including the mentioned correction) gives the estimation of E_{EEET} about 0.37 that means rather high excitation transfer efficiency.

Finally, for the synthesized solution of PS-PPO NP the spectrum of X-ray stimulated luminescence was registered that corresponds to PPO fluorescent emission (**Figure 5**).

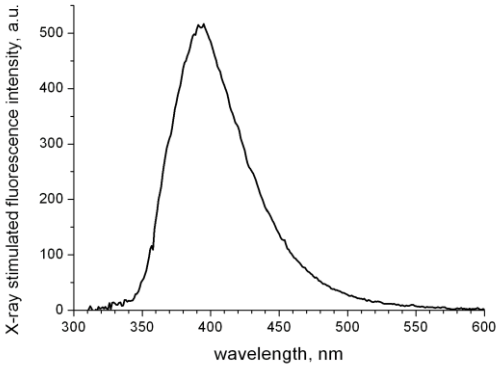

Figure 5. X-ray stimulated luminescence spectrum of PS-PPO NP solution.

The possibility to register this spectrum for the water solution of nanoparticles should be connected with the absorption of X-rays by the atoms of PS matrix (that constitute rather high percent of the solution mass) with further stepwise transition of the excitation energy to the encapsulated PPO molecules.

Conclusions

It was shown that inside the nanoparticles of polystyrene with encapsulated diphenyloxazole molecules, the electronic excitation energy transfer from polystyrene matrix to encapsulated PPO molecules takes place; efficiency of such transfer was roughly estimated to be about 0.37. X-ray stimulated fluorescence of PS-PPO NP was registered.

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